Unit Cell and Optical Properties of $t,t,\Delta^{9,11}$-Linoleic Acid[1]

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In a previous paper[2] $t,t,\Delta^{9,11}$-linoleic acid was characterized by X-ray diffraction patterns of powdered specimens. Optical and X-ray diffraction data for single crystals provide a more detailed characterization of this acid, and these data are reported below.

Optical Properties.—Preparation of $t,t,\Delta^{9,11}$-linoleic acid has been described.[2] Single crystals of the acid were obtained by slow evaporation from xylene at 25°. The crystals were monoclinic and occurred as thin, diamond-shaped plates lying on the orthopinacoid, (100), and bounded by the domes, {011}. Inter-edge angles measured in the plane of the plate were 68° and 112°, both ± 1/2°. Since the X-ray data showed that the monoclinic angle was nearly 90°, the inter-edge angles were nearly equal to the interfacial angles of the dome zone. The axial ratio $b:c$ computed from these angles is 1:1.47, which is in good agreement with the ratio 1:1.48 determined from the X-ray data.

The crystals gave a positive biaxial interference figure; one optic axis was perpendicular to the plate, and the optic axial plane was parallel to the bisector of the acute angle of the plate. The apparent optic axial angle, $2E$, for NaD light was 54° 18′. The optic angle in the crystal was computed to be 34° 46′. The immersion method with NaD light gave 1.527 as the measured value of B.

X-Ray Diffraction Data.—Unit cell dimensions and symmetry elements of $t,t,\Delta^{9,11}$-linoleic acid were determined from diffraction patterns of single crystals taken with a precession camera using copper radiation ($\lambda = 1.539$ kX.). The plane symmetry of zero and n-level patterns placed the crystal in the monoclinic system. Systematic extinction of the general spectra hkl occurred when $h + k$ was odd, and $h0l$ was absent when l was odd, permitting either space group Cc or $C2/c$.

Dimensions of the monoclinic unit cell are $a_0 = 95.69$ kX., $b_0 = 4.95$ kX., $c_0 = 7.31$ kX., and $\beta = 90.6°$. Crystallographic axis a was inclined 0.6° to the plate normal, b bisected the obtuse angle, and c bisected the acute angle of the plate. The observed density of 1.01 is in reasonable agreement with the density, 1.07, computed with the assumption of eight molecules per unit cell.

Crystal Structure.—From the unit cell dimensions and the intensities of the ($h00$) reflections which were observed out to $h = 80$, it is evident that the structure is based on dimeric linoleic acid molecules oriented with their length along the a axis. Since the lattice is C-centered, a_0 (95.69 kX.) corresponds to the projected length of two dimers. The alternation in intensity of the ($h00$) reflections with odd orders strong for $h/2<7$ and even orders strong for $7<h/2<20$ is characteristic of the diffraction patterns of all long-chain saturated fatty acids. No reasonable structures based on space group $C2/c$ were found, and it is likely, therefore, that the structure is based on space group Cc with dimers in the general position.

One can estimate the angle of tilt of the linoleic acid dimer with respect to $[d_{001}]$ from the observation that reflection (80.00) is strong. For this reflection to be intense, the contributions of all atoms must be near their maximum values. Considering only the carbon atoms, which must make the major contribution, and assuming the $t,t,\Delta^{9,11}$-linoleic acid dimer to be planar and centrosymmetrical, and to have normal bond angles and lengths, the principal dependence of F_{h00} on α can be expressed by

$$F_{h00} \sim \frac{1}{1 - \cos(2\pi ht\cos\alpha)}$$

where α is the angle of tilt measured with respect to $[d_{100}]$ and t is the distance between alternate carbon atoms (2.52 kX.) expressed as a fraction of d_{100}. For $h = 80$, the denominator of (1) becomes zero at $\alpha = 18.3°$, and F_{h00} attains its maximum value. The direction of maximum polarizability of the crystal, $''\eta_\gamma$, should lie approximately in the direction of the dimers and thus affords another measure of the angle of tilt. η_γ makes an angle of 17° 23′ with $[d_{100}]$, in good agreement with the value of 18.3° derived from the diffraction data. The conventional "angle of tilt," which is the angle of the dimers with respect to the plane of the carboxyl groups, is $90° - \alpha$, or about 72°.

(1) Taken in part from a thesis submitted by L. P. Witnauer in partial fulfillment of the requirements for a Master of Arts degree at Temple University, June, 1948.

(2) L. P. Witnauer, P. I. Nichols, Jr., and F. R. Senti, *J. Am. Oil Chem. Soc.*, **26**, 653 (1949).

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